Surface Tension of Pure Heavy n-Alkanes and Other Heavy Fluids: A Corresponding States Approach

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ABSTRACT

The surface tension of heavy n-alkanes is a poorly studied subject. Few data exist and the predictive methods used for their estimation are rather complex or show considerable errors for the higher members of the series.

In this work the corresponding states theory is used to predict the surface tension of the series of the n-alkanes. Two approaches have been followed: the first is a second order perturbation model based on a Taylor Series expansion of the surface tension using the Pitzer acentric factor; the second approach uses shape factors to account for the non-conformalities. Comparison of the two models with experimental data and other available predictive methods are presented.

INTRODUCTION

Many engineering applications in the chemical process industry require surface tension data. Some examples include the flow of process streams and the mass-transfer operations such as distillation, extraction, absorption and adsorption.

Especially interested in the surface tension of the series of the n-alkanes is the petroleum industry [1]. It is not unusual in the extraction of crudes to add surfactants to alter the interfacial properties between crude oil and the geological reservoir, to improve production and increase oil yields. This happens because in the petroleum rocks the flow is mainly dominated by the interfacial tension of the crude.

There is a considerable number of n-alkanes from which we can expect to have experimental surface tension data at a given number of temperatures. Although there are enough experimental values for some of the lighter n-alkanes, there are few for other elements of the series, particularly for the heavier ones, and the available data only cover a narrow range of temperature. In fact, surface tension data is lacking at low temperatures and near the critical region.

Good estimation methods are thus required to evaluate surface tension. *Parachor* [2], *Gradient Theory* [3] and *Corresponding States* methods [1,4,5] are the most frequently used. Of these, *Corresponding States* are the simpler, requiring only the detailed knowledge of the reference fluid (or fluids) and of a small number of well defined pure component properties. The coupling between the strong theoretical basis behind *Corresponding States Principle* and the accuracy of the empirical equations used to describe the reference fluid is another reason which justifies the effort in developing such models.

2. Corresponding States Principle

The basic concept of Corresponding States Principle is to apply dimensional analysis to the configurational portion of the statistical mechanical partition function. The end result of this analysis is the expression of residual thermodynamic properties in terms of dimensionless groups.

The original, two-parameter corresponding states principle leads to an equation of state which expresses the residual compressibility factor in terms of a universal function of two parameters, usually the dimensionless temperature and molar volume. Experimental evidence has shown that the two-parameter corresponding states is only obeyed by the noble gases and nearly spherical molecules such as methane, nitrogen and oxygen. In order to extend the corresponding states theory to a larger spectrum of fluids, additional characterization parameters have been introduced to account for the non-conformalities between fluids. Two main approaches have been followed in this parameterisation: the first introduces additional characterization parameters and then performs a multi-parameter Taylor's series expansion of the compressibility factor about the parameters; the second approach is to extend the simple two-parameter corresponding states principle at its molecular origin. This is accomplished by making the intermolecular potential parameters functions of the additional characterization parameters and the thermodynamic state, e.g., the temperature T. The net result is a corresponding states model which has the same mathematical form as the simple two-parameter model, but the definitions of the dimensionless volume and temperature are more complex. The aim of this paper is to explore both of these corresponding states approaches in order to apply them to surface tension calculations.

2.1. Taylor Series Expansion in Pitzer Acentric Factor

The estimation of surface tension using a Taylor series expansion in Pitzer acentric factor has already been proposed [1,5]. The series is truncated beyond the first derivative, giving a linear function:

$$\gamma_{rj} = \gamma_{r1} + \frac{\omega_j - \omega_1}{\omega_2 - \omega_1}\left(\gamma_{r2} - \gamma_{r1}\right) \tag{1}$$

where γ represents the surface tension, j stands for the target fluid and the subscripts 1 and 2 refer to two reference fluid properties. Although the formalism is the same, the literature displays a variety of ways to reduce the surface tension: Rice and Teja [5] use the critical volume and critical temperature, while Zuo and Stenby [1] used the critical pressure and critical temperature.

$$\gamma_r = \gamma \times \frac{V_c^{2/3}}{T_c} \tag{2}$$

$$\gamma_r = \ln\left(\frac{\gamma}{P_c^{2/3}T_c^{1/3}} + 1\right) \tag{3}$$

Other authors [6] proposed a linear form with the critical pressure and critical temperature:

$$\gamma_r = \frac{\gamma}{P_c^{2/3}T_c^{1/3}} \tag{4}$$

In all cases, good agreement with experimental data was obtained in the range of fluids covered by the two selected reference fluids. However, large deviations can be found if an extrapolation of Eq. (1) is attempted, or if the reference fluids are not very far apart in the family sequence. This fact can be observed in Figs. 1 and 2, where the

reduced surface tension for C_1-C_{20}, C_{26}, C_{32} and C_{60}, as a function of the acentric factor shows a clear curvature for the heavier hydrocarbons.

In order to account for these deviations, the Taylor series expansion of the reduced surface tension is carried out to the second order term, thus yielding the following equation

$$\gamma_{rj} = \gamma_{r2} + D_1(\omega - \omega_2) + D_2(\omega - \omega_1)(\omega - \omega_2) \tag{5}$$

where

$$D_1 = \frac{\gamma_{r1} - \gamma_{r2}}{\omega_1 - \omega_2} \tag{6}$$

$$D_2 = \frac{\dfrac{\gamma_{r3} - \gamma_{r2}}{\omega_3 - \omega_2} - \dfrac{\gamma_{r1} - \gamma_{r2}}{\omega_1 - \omega_2}}{\omega_3 - \omega_1} \tag{7}$$

Note that a third reference fluid has to be introduced.

2.2. Extended Corresponding States Theory

In the Extended Corresponding States Theory, the non-conformalities are accounted for by the introduction the additional parameters, the shape factors, in the definitions of the equivalent state point:

$$V = V_0 \, h_x = V_0 \frac{V_j^c}{V_0^c} \phi \qquad\qquad T = T_0 \, f_x = T_0 \frac{T_j^c}{T_0^c} \theta \tag{8}$$

where h_x and f_x are the equivalent substances reducing ratios and θ and ϕ the shape factors. The shape factors are weak functions of the reduced temperature and, in principle, of the reduced density. They are evaluated by solving simultaneously any two equations relating the thermophysical property of the target and the reference fluid. Usually the compressibility factor and the Helmholtz energy are used. Several review papers have been published that focus on this approach, the most extensive of which are that of Leland and Chappelear [7], Rowlinson and Watson [8] and Mentzer *et al.* [9].

In order to apply this theory to evaluate surface tension, Murad [4] calculated shape factors by the simultaneous solution of the reduced compressibility factors and the reduced surface tensions. The values of these shape factors were then fitted to functions of the temperature and density, using the formulae proposed by Leach *et al.* [5]. Finally the surface tension of the target fluid is calculated from the reference fluid using

$$\gamma_j = \frac{f_j}{h_j^{2/3}} \times \gamma_0 (T_{rj} / \theta) \qquad (9)$$

This procedure has the disadvantage of yielding shape factors that are not the same of those obtained by solving the compressibility factor and the Helmholtz energy. Since, theoretically these shape factors should be the same, recalculation of these shape factors showed that this difference is due to the lack of accuracy of the data available at that time. Another weak point of the model proposed by Murad is the fixed reference fluid, methane, which does not allow accurate predictions for heavy n-alkanes.

Following Cullick and Ely [10], Marrucho and Ely [8] proposed a new predictive method for the determination of the shape factors along the saturation boundary. Using the Frost-Kalkwarf-Thodos equation [12] to describe the saturation pressure and the

Rackett equation [12] for the saturated liquid density, the expressions for the shape factors are:

$$\theta = \frac{1 - C_{r0} + 2\left(1 - T_{rj}\right)^{2/7} \ln\left(Z_{cj}/Z_{c0}\right) - \Delta B_r + \Delta C_r \ln T_{rj} + B_{rj}/T_{rj}}{1 - C_{r0} + B_{r0}/T_{rj}} \tag{10}$$

$$\phi = \frac{\left(Z_{cj}\right)^{\left(1 - T_{rj}\right)^{2/7}}}{\left(Z_{c0}\right)^{\left(1 - T_{rj}/\theta\right)^{2/7}}} \tag{11}$$

where:

$$B_r = -6.207612 - 15.37641\,\omega - 0.574946 \times 10^{-\omega} \tag{12}$$

$$C_r = 8/3 + 9B_r/(5\ln 10) \tag{13}$$

$$\Delta B_r = B_{rj} - B_{r0} \tag{14}$$

$$\Delta Cr = C_{rj} - C_{r0} \tag{15}$$

Although this is a predictive approach, if vapor pressure and liquid density data are available, Z_c and the exponent in the Rackett equation can be treated as adjustable parameters and B_r and C_r can be found by a correlation scheme.

3. Results

Although a considerable amount of data exists, special care has been taken in its selection since very often the values differ considerably from author to author [13-23]. The data reported by Jasper *et al.* [17,19,20] and by Grigoryev *et al* [18], the last covering all the liquid region of some lighter n-alkanes, between C_5 and C_8, were used

preferentially. Eq. (16) was used correlate the experimental surface tension values of the reference fluids for both methods, thus yielding two parameters per each fluid:

$$\gamma = A \times (1 - Tr)^B \qquad (16)$$

The reduction of the surface tension values obtained with this equation was attempted Eqs. (2), (3) and (47). Despite the critical volume usually having a large error associated, the results showed that Eq. (2) was the best choice.

The experimental values of the critical properties and acentric factor were used when available [24-28]. Otherwise correlations for critical temperature [25], critical volume [26], critical pressure [27] and acentric factor [28] were used.

For the Taylor series expansion, a system of 3 reference fluids is needed. This selection is not an easy task since the data from different authors often present wide discrepancies among themselves. For the purpose of this work n-hexane, n-undecane and n-pentadecane were chosen as references because there is enough accurate experimental data and they described well the entire series of n-alkanes.

The proposed model, Eq. (5), was tested for 320 surface tension values for the n-alkane's family and an average absolute deviation (AAD) of 1.14% was obtained (Table 1). In Fig. 3., comparisons of this model with the one proposed by Rice and Teja [5] are presented. It can clearly be seen that the new model improves the surface tension calculation especially for heavy n-alkanes.

The surface tension values calculated using the shape factors from Eqs. (10) and (11), for several n-alkanes, C2-C20, C26 and C32 are compared with experimental results in Table2. An average absolute deviation of 3.7% was obtained. The selected

reference fluids were n-pentane for the range C_2-C_7, n-decane for C_8-C_{12} and C_{15} for those n-alkanes with more than 12 carbon atoms. Surface tension for n-hexacontane was not predicted due to the lack of a suitable reference fluid. Some large deviations were found for the first elements of the series, but we should remember that experimental surface tension of some fluids, like propane and n-butane, present some scatter.

When using this approach, especial care should also be presented in the choice of the reference fluid. The "good" reference fluid should be structurally similar with the target fluid and have a broad range of surface tension values, if possible from the triple point up to close to the critical temperature.

The two proposed models, the Taylor series expansion and the shape factor models, are compared with each other for n-heptane in Figs. 4 and 5. As it was expected the Taylor series expansion gives better predictions than the shape factors model. This is mainly due to the larger number of reference fluids used in the first model Nevertheless, both these model present more accurate values than the other models proposed so far.

4. Summary and Conclusions

Two new corresponding states predictive models were proposed for the determination of the surface tension of a large number of pure n-alkanes at a considerable range of temperatures. The Pitzer acentric factor Taylor series expansion was extended to include a third reference fluid and a group of reference fluids were proposed for the determination of the surface tension with an average absolute error of 1.14%.

The extended corresponding states theory was also suggested for the determination of surface tension, this time with the possibility of selecting an adequate reference fluid

and given a minimum amount of information: critical temperature, critical volume, critical compressibility factor and acentric factor of the reference and the target fluid, as well as some surface tension data of the reference fluid. Although this last approach has given a great deviation, using the same number of reference fluids to predict the studied number of n-alkanes, it is much more simple to use and involves less information. More work will be done on this model to improve its accuracy.

Some surface tension measurements will also be made to increase the number of available experimental data and to improve the predictions.

LIST OF SYMBOLS

f   equivalent substance reducing ratio for temperature

h   -equivalent substance reducing ratio for volume

P   -pressure

R   - gas constant

T   -absolute temperature

V   -volume

Z   -compressibility factor

Z_{ra} - *Rackett* compressibility factor

Greek Letters

ϕ -volume shape factor

γ - surface tension/mN.m^{-1}

λ_i -characterization parameters for extending the simple two-parameter CST

θ -energy shape factor

ω -Pitzer acentric factor

Subscripts

r -reduced property (dimensionless)

c -critical value

j -target or working fluid

0 -reference fluid

l -liquid state

Superscripts

* -reduced property (dimensionless)

sat- saturation property

Table 1

Evaluation of the 2º order perturbation model for surface tension

Substance	AAD(%)	nº of points	T range/K
Ethane	0.96	23	129.2-273.50
Propane	2.94	22	202.15-312.6
n-butane	4.60	20	238.0-318.5
n-pentane	1.47	18	144.8-407.25
n-heptane	0.53	26	183.21-459.18
n-octane	1.53	20	218.51-501.27
n-nonane	0.31	13	273.15-393.15
n-decane	0.33	13	273.15-393.15
n-dodecane	0.22	13	273.15-393.15
n-tridecane	0.23	13	273.15-393.15
n-tetradecane	0.20	12	283.15-393.15
n-hexadecane	0.98	11	293.15-393.15
n-heptadecane	0.76	10	303.15-393.15
n-octadecane	0.21	10	303.15-393.15
n-nonadecane	1.24	11	293.15-393.15
n-eicosane	0.19	11	293.15-393.15
n-hexacosane	2.73	1	343.15-453.15
n-dotriacontane	2.26	11	346.35-422.45
n-hexacontane	5.48	7	383.15-453.15

Table 2

Evaluation of the new predictive ECST model for surface tension

| Substance	AAD(%)	nº of points	T range/K
Ethane	5.9	23	129.2-273.50
Propane	6.7	22	202.15-312.6
n-butane	9.0	20	238.0-318.5
n-hexane	1.7	21	175.12-447.13
n-heptane	3.5	26	183.21-459.18
n-octane	3.8	20	218.51-501.27
n-nonane	0.6	13	273.15-393.15
n-undecane	0.5	13	273.15-393.15
n-dodecane	2.6	13	273.15-393.15
n-tridecane	1.5	13	273.15-393.15
n-tetradecane	0.3	12	283.15-393.15
n-hexadecane	1.7	11	293.15-393.15
n-heptadecane	1.4	10	303.15-393.15
n-octadecane	1.0	10	303.15-393.15
n-nonadecane	1.7	11	293.15-393.15
n-eicosane	5.7	11	293.15-393.15
n-hexacosane	6.6	1	343.15-453.15
n-dotriacontane	13.0	11	346.35-422.45

FIGURE CAPTIONS:

Figure 1: Reduced Surface Tension for n-alkanes as a function of acentric factor (Equation 2) at Tr=0.49.

Figure 2: Reduced Surface Tension for n-alkanes as a function of acentric factor (Equation 3) at Tr=0.49.

Figure 3: Comparison of reduced Surface Tension as a function of acentric factor for the linear (Rice and Teja [5]) and the 2nd order perturbation model.
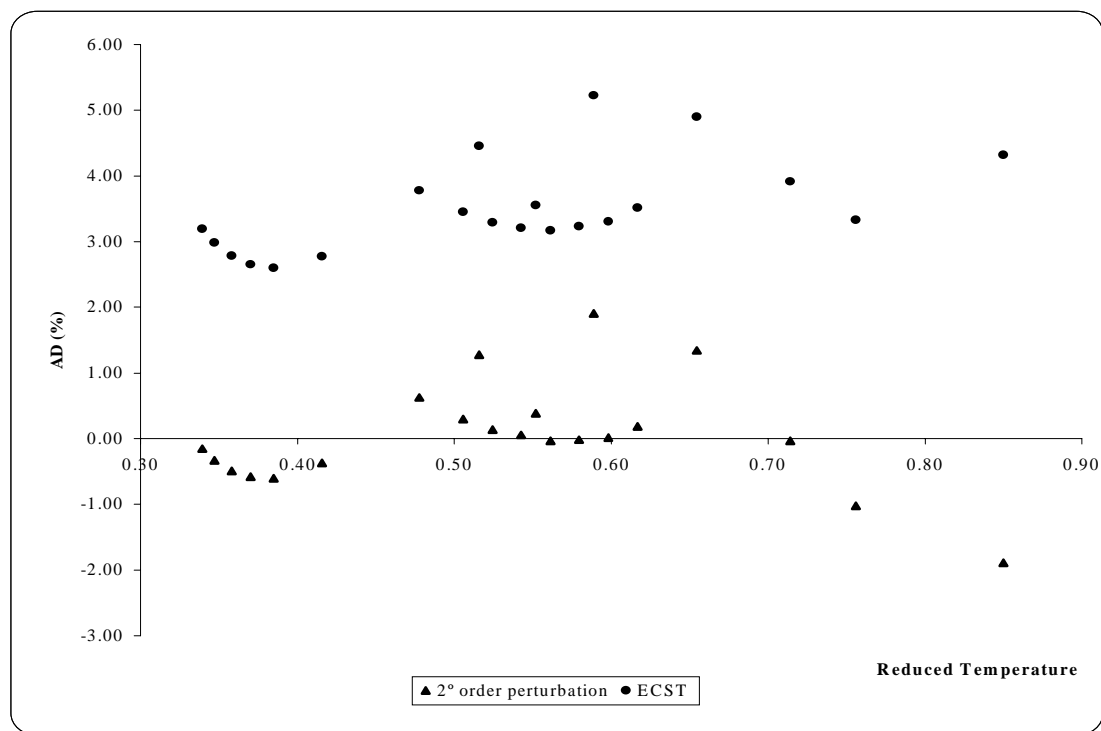
Figure 4: Graphical presentation of experimental and predicted values of surface tension of n-heptane using the new predictions.

Figure 5: Percent average deviation in the surface tension of n-heptane using the new predictions.
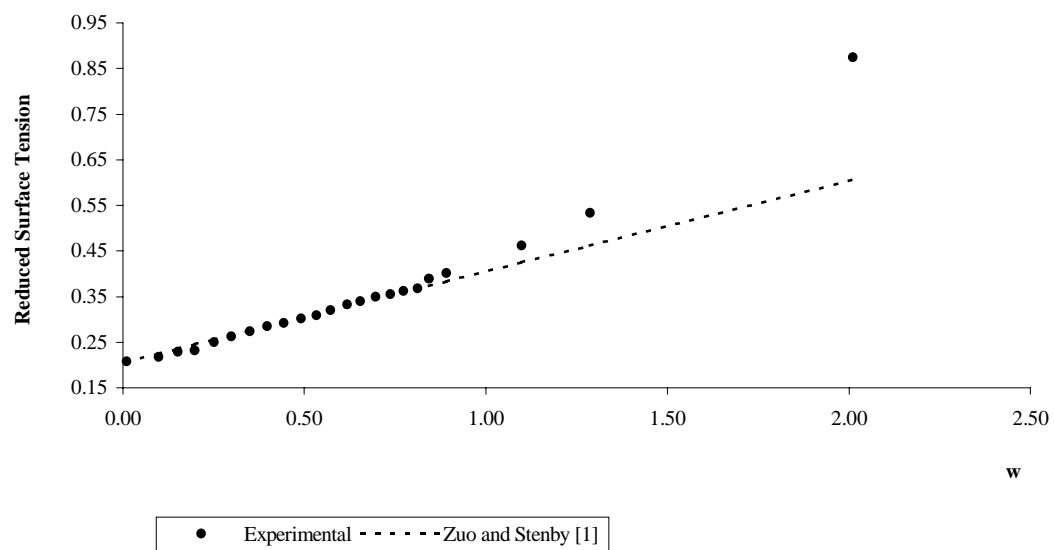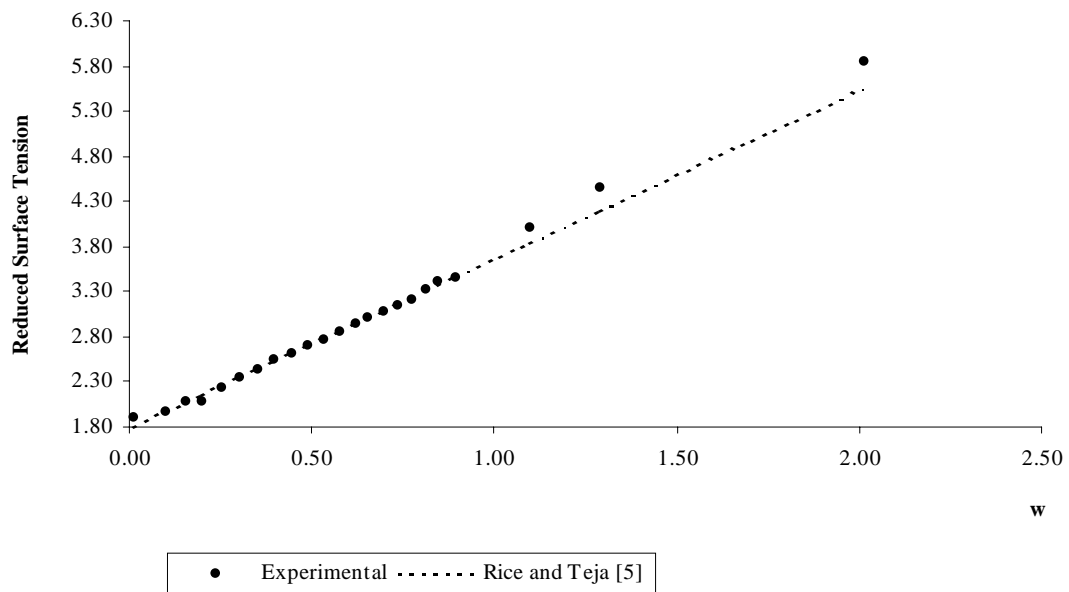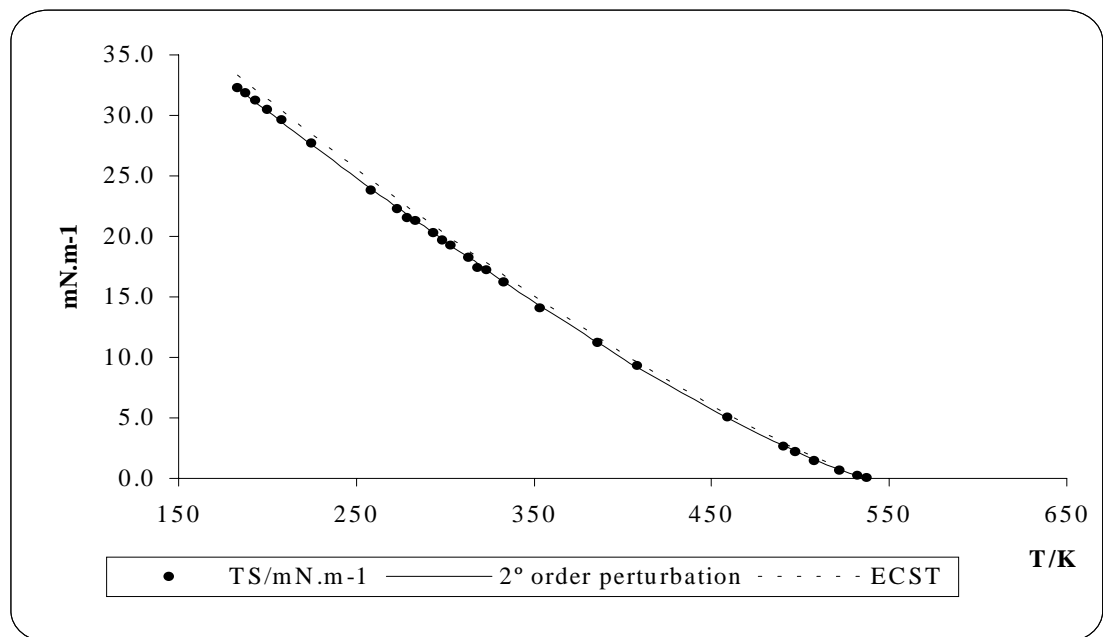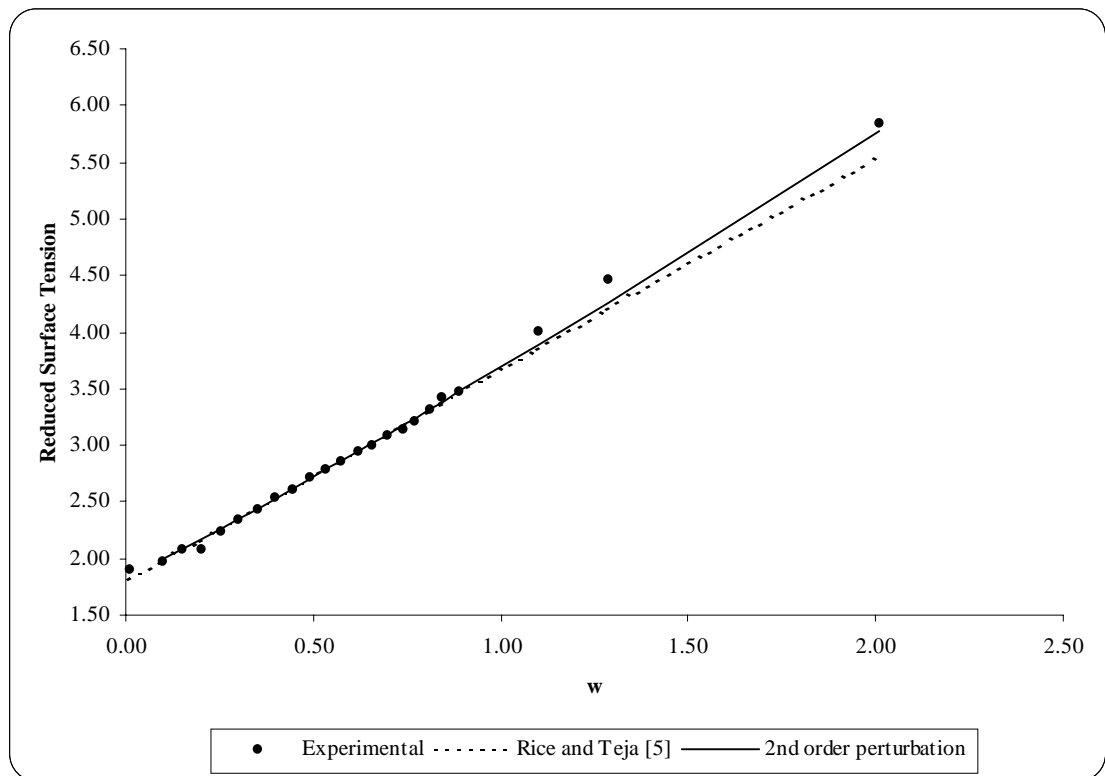
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